N 𝑥64-24024
Code 1   Cat. 21
NASA CR 52851

CORNELL AERONAUTICAL LABORATORY, INC.
BUFFALO 21, NEW YORK

PROJECT FOG DROPS
INVESTIGATION OF WARM FOG PROPERTIES AND FOG MODIFICATION CONCEPTS

3rd QUARTERLY PROGRESS REPORT

CONTRACT NO. NASr - 156
CAL REPORT NO. RM-1788-P-3

OTS PRICE

I AUGUST 1963 - I NOVEMBER 1963

XEROX $ 1.60ph

MICROFILM $ _____

Prepared for:

OFFICE OF AERONAUTICAL RESEARCH
NATIONAL AERONAUTICS AND SPACE ADMINISTRATION
WASHINGTON 25, D.C.

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I. INTRODUCTION

The Office of Aeronautical Research of the National Aeronautics and Space Administration has authorized this Laboratory, under Contract No. NASr-156, to investigate warm fog properties and possible fog modification concepts. The principal objectives of the first year's research effort are to:

1. Construct models of the micro- and macroscopic properties of warm fogs.

2. Define the chemical, physical, and electrical characteristics of fog droplets and explore means of favorably altering these properties.

3. Perform selected laboratory experiments aimed at accelerating the growth or evaporation rate of otherwise stable aerosol droplets.

4. Translate the above findings into feasible concepts of fog modification at air terminals.

This report briefly describes accomplishments of the period 1 August - 1 November 1963, and outlines plans for the next quarter.

II. ABSTRACT

During the quarter, the effects of fatty alcohol monolayers on water droplets and on condensation nuclei (N_aCl cyrstals) were studied. The degree of retardation of growth (evaporation) of monolayer treated drops is dependent upon (1) material type, (2) compression of the monolayer, and (3) absence of film impurities. Preliminary tests suggest that condensation nuclei activity can be influenced by monolayer materials.

Study of droplets treated with ionic surfactants was commenced. Meteorlogical analysis of a Buffalo fog provided further insight into the dynamics of fog formation.

III. DISCUSSION

1. Monolayer Effect on Droplet Growth

Certain surface-active monolayers, such as the fatty-alcohols hexadecanol and octadecanol, are well known retardants of water evaporation when spread on ponds and reservoirs. As discussed in prior quarterly reports, our theoretical and experimental efforts have shown that these monolayers also tend to inhibit condensation of water vapor on droplets (i.e. retard diffusional droplet growth) in a super-saturated environment. It was suggested that monolayer treatment of a portion of a fog droplet population might result in the favorable alteration of the size distribution of fog droplets.

During the last quarter, studies were made of (1) the behavioral properties of monolayers when applied to water droplets and (2) the feasibility of certain droplet treatment techniques. The monolayers that we experimented with are given in Table I along with some of their basic properties; the alcohols were prepared in powder and in liquid form and spread on water.

Table I Monolayers Properties

	Formula	Density g/ml	Melt. Pt.	Boil. Pt.	Solubility in water	alc./ether
1. Hexadecanol (cetyl alcohol)	$CH_3(CH_2)_{15}OH$	0.817	$49.3^{\circ}C$	$190^{\circ}C$	i	s
2. Octadecanol (stearyl alcohol)	$CH_3(CH_2)_{16}CH_2OH$	0.812	59	210.5	i	s
3. Stearic Acid	$CH_3(CH_2)_{16}COOH$	0.847	69.4	283	.0348/100ml	s

It is known that these long chain molecules possess a hydrophilic component (hydroxyl OH ion or a carboxyl COOH ion) and a hydrophobic component (hydrocarbon). When in contact with water, the rod-like molecule aligns itself perpendicular to the surface so that the hydrophilic "head" seeks the water interface and the hydrophobic "tail" lies above. The hydrophobic "tails" of oriented molecules constitute the barrier to water vapor penetration. As Langmuir et al. (1943) showed, such a single layer of material or monolayer is far more effective as a water barrier than multiple layers haphazardly oriented.

The effectivness of a monolayer in retarding evaporation, or in retarding condensation, is a function of the material involved and the compression of the monolayer. The term compression refers to the spacing of molecules in the monolayer film. Figure 1, taken from Barnes and La Mer (1962), shows the dependence of water-evaporation resistance on surface pressure for monolayers spread on water reservoirs. Surface pressure, the customarily used measure of film compression, is a quantity with dimensions of force per unit length and is numerically equal to the difference in surface tension of water and of the film. Our laboratory experiments with droplets, rather than plane water surfaces, suggest that the resistance to droplet growth offered by monolayers of hexadecanol and octadecanol follow similar trends to those indicated in Figure 1.

Three features of the curves are particularly noteworthy:

a. The specific evaporation resistance R (droplet growth resistance) of a fatty alcohol monolayer increases with compression of the film. This trend continues to a maximum surface pressure of about 50 dynes/cm, above which the film ruptures and R drops sharply. Though not shown, the R for stearic acid generally levels off with increasing F.

b. Octadecanol, though more difficult to spread on water, is considerably more effective in inhibiting evaporation than haxadecanol.

c. A mixture of octadecanol and hexadecanol is more effective than either single substance at low levels of film surface pressure (F < 12 dynes/cm). This is particularly important in our potential application to fog droplets where we may not be able to exercise wide control of film pressure. Our experiments suggest that it may be difficult to achieve the high surface pressures corresponding to very compact monolayers.
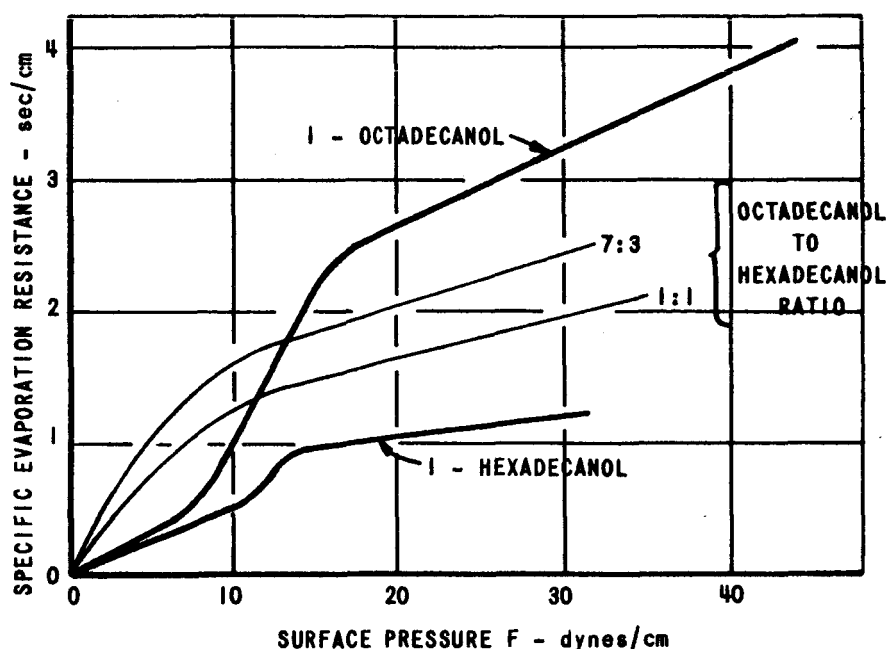

Figure I RESISTANCE TO EVAPORATION OF A PLANE WATER SURFACE COATED WITH A MONOLAYER
(Barnes and LaMer, 1962)

When dealing with monolayers on a flat surface, it is relatively simple to increase film pressures merely by mechanically compressing the film between movable walls or floats. With small droplets, this approach is not tenable. In our laboratory experiments, droplets were extracted on fine quartz probes from beakers of water, the water surface having been coated with a monolayer in the droplet extraction process. Some of the monolayer was also captured. Film compression was achieved by causing partial droplet evaporation to take place, thereby decreasing the surface area of a treated droplet. One can also vary film pressure, within limits, by varying the quantity of monolayer material dispersed on water; our measurements of surface tension, employing the ring method and drop-weight method, indicate that the maximum film pressure that can be achieved by increasing the amount of hexadecanol and/or octadecanol is approximately 30-35 dynes/cm.

It has been established that solution impurities, among them certain salts and benzene, constitute "holes" in a monolayer through which water vapor can readily penetrate. The resistance to water penetration of such impurities and of the film are analogous to parallel resistance in electrical circuits. Thus, a monolayer with "holes" equivalent to 1% of its surface area may have its water evaporation resistance reduced by approximately 90 to 99% (La Mer, 1962). Frequently, impurities can be squeezed out of a monolayer by compressing the film, a laboratory option that does not presently appear transferrable to free atmosphere applications. However, since the postulated fog alteration technique relies on <u>selective</u> monolayer treatment of droplets, the presence of droplet impurities in fogs may provide a built-in selection scheme. Further analysis of fog nuclei characteristics and their effects on monolayers are necessary.

Our findings to date on controlling droplet growth with monolayers can be summarized as follows:

a.   The droplet evaporation equation (Fuchs, 1959 and Eisner, Quince, and Slack, 1960):

$$dm/_{dt} = \frac{4\pi\,MD}{RT}\,(f\,P_T - P_\theta)\,\frac{a}{(1 = D/av\alpha)}$$

is valid for droplet growth under super-saturated conditions.

$\dfrac{dm}{dt}$	is the rate of evaporation or growth (g/sec) of a droplet of radius a.
M	the molecular weight of the liquid.
D	the diffusion coefficient for the vapor into the air
f	the relative humidity expressed as a fraction
P_T	the vapor pressure of the liquid at the ambient absolute temperature T
P_θ	the vapor pressure of the liquid at the droplet temperature
R	the universal gas constant
v	molecular mobility equal to $(RT/2\pi M)$
α	the coefficient of evaporation (or condensation)

Under ideal laboratory conditions, the condensation coefficient α may be markedly decreased by the monolayer with a corresponding decrease (10^2 to 10^4) in droplet growth rate.

b.   The degree of inhibition of droplet growth obtained is strongly dependent upon (1) compression of the monolayer film, (2) type of monolayer employed and (3) the presence (absence) of impurities.

c.   To date, our most consistent laboratory results have been achieved with monolayers prepared from a mixture of hexadecanol and octadecanol crystals. The mixture provides comparatively high values of resistance to droplet growth for only modest degrees of film compaction.

d. Impurities that become trapped within a monolayer can completely negate the desired condensation retardation effect. Benzene, which formerly was used as a solvent for liquid dispersal of these fatty alcohols, constitutes such an impurity. Our data indicate that methyl alcohol is another deleterious solvent; petroleum ether is a satisfactory solvent. Salts and chemical compounds found in the atmosphere would undoubtedly vary the degree of effectiveness of monolayers.

2. Condensation Nuclei Deactivation

A related hypothesis for increasing the ultimate size of fog droplets is to deactivate a percentage of the condensation nuclei found in the free atmosphere just prior to fog occurrence; the resultant fog might then consist of fewer, larger particles with less severe visibility characteristics. Hence, preliminary experiments were conducted to determine if hygroscopic condensation nuclei could be coated with fatty alcohol monolayers to prevent or retard condensation of water on the nuclei. Sodium chloride (N_aCl) crystals, a common type of atmospheric condensation nucleus, were coated in various ways with a mixture of hexadecanol and octadecanol and tested.

One coating method involved dissolution of N_aCl crystals in a liquid monolayer suspension and also in plain water. The salt crystals were recovered from the saline solutions by drying; drying time was substantially prolonged by the monolayer, thus attesting to the potential effectiveness of monolayers on N_aCl solution droplets. After complete drying, the crystals were subjected to relative humidities of 90 to 100%. The rates of subsequent deliquescence of treated and untreated salt crystals were compared; no measureable difference could be detected.

Another coating method involved dusting of N_aCl crystals with powdered octadecanol and hexadecanol. Some crystals were similarly coated with kaolin powder -- a non-hygroscopic inert clay material -- to simulate the simple physical barrier to diffusion that might be created by the alcohol powder.

The subsequent rate of deliquescence of untreated N_aCl crystals and of N_aCl crystals powdered with kaolin were comparable. However, the deliquescence rate of N_aCl crystals coated with octadecanol and hexadecanol powder was retarded; total dissolution time of equal sized crystals was increased by a factor of three.

These preliminary results warrant further analysis of nuclei deactivation techniques and consideration of other classes of surface films.

3. Ionic Surfactants

Numerous investigators have suggested that coalescence of droplets of an aerosol might be increased by selective surface charging of the droplets. Elton (1953) has postulated the use of ionic surface-active agents to alter droplet surface charge in fog. Similarly, it is conceivable that the diffusional growth rate of water droplets will be influenced by ionic surfactants (Benton, et al., 1958).

In order to assess both the diffusional and coalescent growth rates of droplets treated with ionic fluids, a number of tergitol surfactants were obtained from the Union Carbide Co. as follows:

Anionic[*]	Cationic[*]	Non-ionic
Sodium Heptadecyl Sulfate	Amine 220	3 types of nonyl phenyl
Sodium Tetradecyl Sulfate		poly-ethylene glycol
Sodium 2-Ethylhexyl Sulfate		ether

We have just commenced to measure the <u>diffusional</u> growth rate of individual droplets treated with the above surfactants in our cloud diffusion chamber. Figure 2 depicts two initial experimental runs. As shown, no significant change in the theoretical diffusional growth rate of water droplets has thus far been observed.

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[*]An anionic substance bears a negative charge and seeks a positive pole (anode).
A cationic substance bears a positive charge and seeks a negative pole (cathode).

SOLID CURVES ARE THEORETICAL DROPLET GROWTH RATES FOR
UNTREATED DROPLETS

O "PLAIN" WATER DROPLET
△ DROPLET COATED WITH CATIONIC SURFACTANT
□ DROPLET COATED WITH ANIONIC SURFACTANT
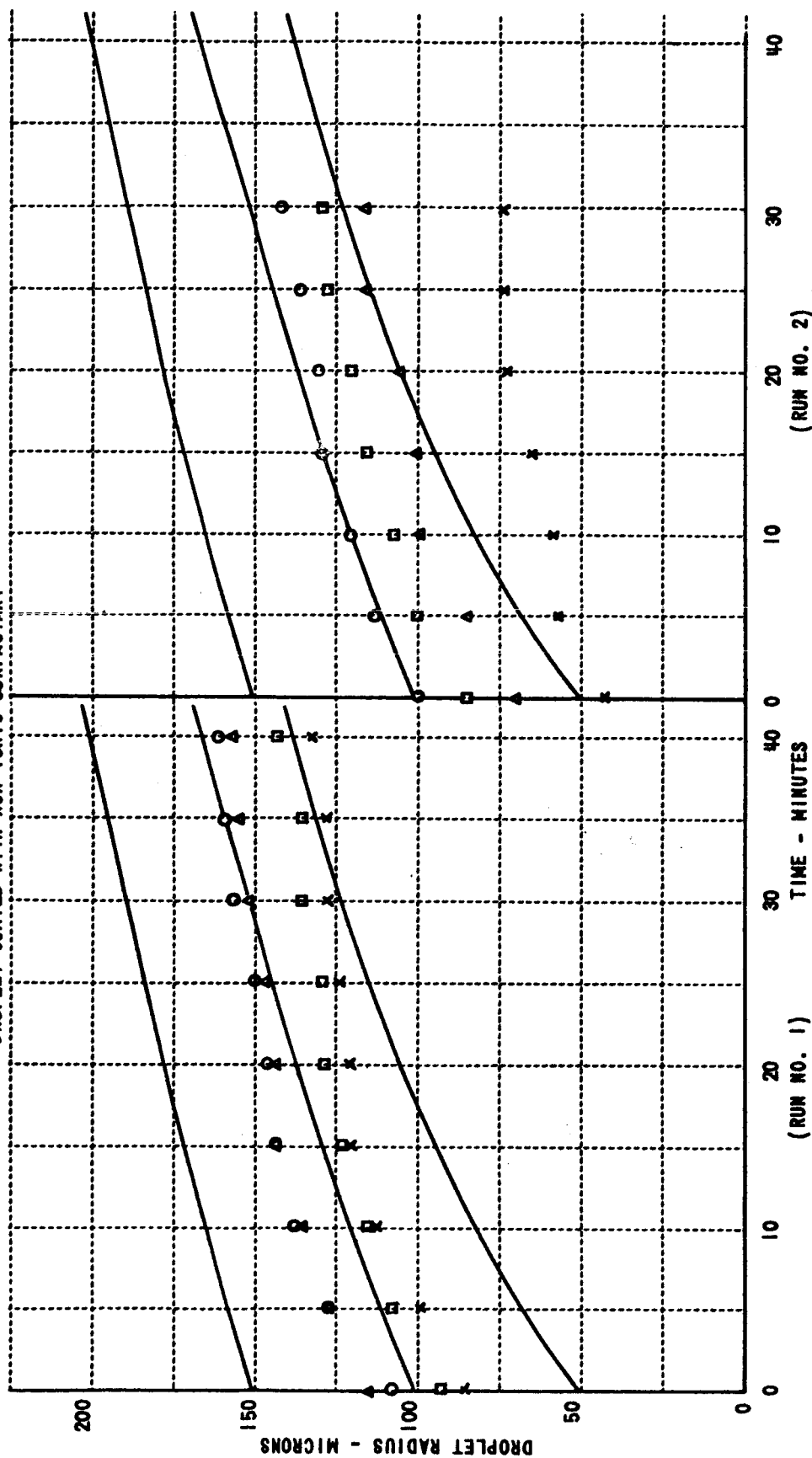✕ DROPLET COATED WITH NON-IONIC SURFACTANT

Figure 2 DROPLET GROWTH RATE IN A CHEMICAL DIFFUSION
CLOUD CHAMBER -- SUPERSATURATION = 2.9%

9

4. Dynamic Fog Model

The dynamic fog model study has been continued with the analysis of a fog which occurred in Buffalo on May 14, 1963. The equations presented in the first quarterly report were applied to the local Weather Bureau observations taken in the May fog. Since the actual liquid water content of the fog is not known, it was not possible to make a complete analysis. However, certain conclusions were suggested.

The Buffalo fog was of the advection type. It was preceded by overcast skies which should have minimized the effects of radiational cooling; the wind speed exceeded 10 knots throughout the period of fog. The temperature differences between the surface and the fog top was less than $2^{\circ}C$ at the time of observation. A process of pure vertical mixing, operating within this temperature gradient, could lead to fog with a maximum liquid water content of 20 mg/m^3. When compared to typical advection fog water contents of 170 mg/m^3 (as per our physical fog model), it is clear that mixing alone could not have produced the dense fog observed.

Since the simplified boundary-layer mixing model (Rodhe 1962) cannot explain the fog chosen for study, it appears that factors not included in the model may be important. In particular, the model requirement that the liquid water content at the surface of the ground be zero may be incorrect for some types of fog. This requirement greatly restricts the amount of liquid water that can be produced at any level through mixing. The possible role of hygroscopic condensation nuclei in initiating fog and maintaining it near the surface should be considered. When such nuclei are present, a fog could begin to form over a cold surface (at relative humidities less than 100%) before water begins to condense on the ground. Subsequent mixing would provide vapor which could be used for growth of droplets, rather than condensation on the cold surface. We plan to assess the role of hygroscopic nuclei in fog formation. If such nuclei are instrumental in enhancing the water content of fogs, the aforementioned nuclei deactivation effort assumes added importance.

IV. FUTURE PLANS

During the coming quarter, we plan to conduct the following work:

1. Continue the study of monolayer treatment of aerosol droplets and condensation nuclei.

2. Define the effect of ionic surfactants on diffusional and coalescent growth of droplets.

3. Perform a brief climatological study of supercooled fog occurrence in the United States.

4. Briefly review warm fog modification concepts generated on this and other programs with recommendations for future promising research.

5. At the conclusion of the report period, commence preparation of a detailed annual summary report.

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